Claims

What is claimed is:

- 1. A negative photoresist composition, comprising:
 - (a) a radiation sensitive acid generator;
 - (b) an additive having the structure:

wherein R_1 represents one of hydrogen, an alkyl group, an aryl group, a semi- or perfluorinated alkyl group, a semi- or perfluorinated alkaryl group, an aralkyl group, and a semi- or perfluorinated arkyl group, an aralkyl group, and a semi- or perfluorinated aralkyl group,

wherein R₂ represents one of hydrogen and a straight or branched alkyl group with 1 to 50 carbons,

wherein R₃, R₄, and R₅ independently represent one of hydrogen and a straight or branched alkyl group with 1 to 6 carbons; and

(c) a resist polymer comprising a repeating first monomer unit derived from a first monomer comprising the structure:



wherein M is a polymerizable backbone moiety,

wherein Z represents one of -C(O)OR-, -C(O)R-, -OC(O)R-, -OC(O)-C(O)OR-, an alkylene group, an arylene group, a semi- or perfluorinated alkylene group, and a semi- or perfluorinated arylene group,

wherein R represents one of an alkylene group, an arylene group, a semi- or perfluorinated alkylene group, and a semi- or perfluorinated arylene group,

wherein p is 0 or 1,

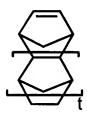
wherein the resist polymer is soluble in an aqueous alkaline developer solution,
wherein the acid generator is adapted to generate an acid upon exposure to imaging
radiation characterized by a wavelength, and

wherein the resist polymer is adapted to chemically react with the additive in the presence of the acid to generate a product that is insoluble in the developer solution.

- 2. The negative photoresist composition of claim 1, wherein at least one of R_1 and R_2 includes one or more alicyclic structures.
- 3. The negative photoresist composition of claim 1, wherein the additive comprises N-methoxymethyl cyclohexanecarboxamide or N-methoxymethyl 1-adamantanecarboxamide.

4. The negative photoresist composition of claim 1, wherein the polymerizable backbone moiety, M, includes one of a first structure and a second structure, wherein the first structure is:

wherein R₆ represents one of hydrogen, an alkyl group of 1 to 20 carbons, a semi- or perfluorinated alkyl group of 1 to 20 carbons, and CN, and wherein the second structure is:



wherein t is an integer from 0 to 3.

- 5. The negative photoresist composition of claim 1, wherein the resist polymer further comprises a second monomer unit derived from a second monomer having an aqueous base soluble moiety.
- 6. The composition of claim 5, wherein the second monomer comprises at least one of a fluorosulfonamide and a carboxylic acid moiety.

- 7. The negative photoresist composition of claim 1, wherein the radiation sensitive acid generator comprises at least one of an onium salt, a succinimide derivative, a diazo compound, and a nitrobenzyl compound.
- 8. The negative photoresist composition of claim 7, wherein the acid generator comprises at least one of 4-(1-butoxynaphthyl) tetrahydrothiophenium perfluorobutanesulfonate, triphenyl sulfonium perfluorobutanesulfonate, t-butylphenyl diphenyl sulfonium perfluorobutanesulfonate, 4-(1-butoxynaphthyl) tetrahydrothiophenium perfluorooctanesulfonate, triphenyl sulfonium perfluorooctanesulfonate, t-butylphenyl diphenyl sulfonium perfluorooctanesulfonate, di(t-butylphenyl) iodonium perfluorobutane sulfonate, di(t-butylphenyl) iodonium perfluoroethylcyclohexane sulfonate, di(t-butylphenyl) iodonium perfluoroethylcyclohexane sulfonate, di(t-butylphenyl)iodonium camphoresulfonate, and perfluorobutylsulfonyloxybicylo[2.2.1]- hept-5-ene-2,3-dicarboximide.
- 9. The negative photoresist composition of claim 1, further comprising at least one of a solvent and a quencher.
- 10. The negative photoresist composition of claim 9, wherein the solvent comprises at least one of an ether, a glycol ether, an aromatic hydrocarbon, a ketone, and an ester.
- 11. The negative photoresist composition of claim 9, wherein the solvent comprises at least one of propylene glycol monomethyl ether acetate, ethyl lactate, γ -butyrolactone, and cyclohexanone.

- 12. The negative photoresist composition of claim 9, wherein the quencher comprises at least one of an aromatic amine, an aliphatic amine, and a tetraalkyl ammonium hydroxide.
- 13. The negative photoresist composition of claim 9, wherein:

the weight of the polymer is about 1% to about 30% of the weight of the composition; the weight of the solvent is about 70% to about 99% of the weight of the composition; the weight of the additive is about 5% to about 70% of the weight of the polymer; and the weight of the acid generator is about 0.5% to about 20% of the weight of the polymer.

- 14. The negative photoresist composition of claim 13, further comprising a quencher, wherein the weight of the quencher is about 0.1% to about 1.0 wt. % of the weight of the polymer.
- 15. The negative photoresist composition of claim 9, wherein:

the weight of the polymer is about 5% to about 15% of the weight of the composition; the weight of the solvent is about 85% to about 95% of the weight of the composition; the weight of the additive is about 10% to about 50% of the weight of the polymer; and the weight of the acid generator is about 0.5% to about 15% of the weight of the polymer.

- 16. A method of patterning a substrate, said method comprising the steps of:
- (A) applying a negative photoresist composition to the substrate to form a resist layer on a material layer of the substrate and in direct mechanical contact with the material layer, said composition comprising:
 - (a) a radiation sensitive acid generator;
 - (b) an additive having the structure:

wherein R₁ represents one of hydrogen, an alkyl group, an aryl group, a semi- or perfluorinated alkyl group, a semi- or perfluorinated alkaryl group, an aralkyl group, and a semi- or perfluorinated aralkyl group,

wherein R_2 represents one of hydrogen and a straight or branched alkyl group with 1 to 50 carbons,

wherein R₃, R₄, and R₅ independently represent one of hydrogen and a straight or branched alkyl group with 1 to 6 carbons, and

(c) a resist polymer comprising a repeating first monomer unit derived from a first monomer comprising the structure:

wherein M is a polymerizable backbone moiety,

wherein Z represents one of -C(O)OR-, -C(O)R-, -OC(O)R-, -OC(O)-C(O)OR-, an alkylene group, an arylene group, a semi- or perfluorinated alkylene group, and a semi- or perfluorinated arylene group,

wherein R represents one of an alkylene group, an arylene group, a semi- or perfluorinated alkylene group, and a semi- or perfluorinated arylene group,

wherein p is 0 or 1, and

wherein the resist polymer is soluble in an aqueous alkaline developer solution;

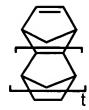
(B) selectively exposing a first portion of the resist layer to imaging radiation characterized by a wavelength such that a second portion of the resist layer is not exposed to the radiation, wherein the first and second portions of the resist layer form a pattern in the resist layer, wherein the radiation causes the acid generator to generate acid in the first portion of the resist layer, wherein the acid facilitates a chemical reaction between the resist polymer and the additive in the first portion of the resist layer such to generate a reaction product in the first portion of the resist layer, and wherein the reaction product is insoluble in the developer solution; and

- (C) developing away the second portion of the resist layer by contacting the resist layer with the developer solution such that the second portion of the resist layer is replaced by voids in the resist layer.
- 17. The method of claim 16, further comprising the steps of:
- (D) transferring the pattern in the resist layer to the material layer, by etching into the material layer through the voids in the resist layer; and
 - (E) after step (D), removing the resist layer.
- 18. The method of claim 16, wherein the wavelength less than or equal to about 193 nm.
- 19. The method of claim 16, wherein the wavelength is about 157 nm.
- 20. The method of claim 16, wherein the wavelength is about 193 nm.
- 21. The method of claim 16, wherein at least one of R₁ and R₂ includes one or more alicyclic structures.
- 22. The method of claim 16, wherein the additive comprises N-methoxymethyl cyclohexanecarboxamide or N-methoxymethyl 1-adamantanecarboxamide.

23. The method of claim 16, wherein the polymerizable backbone moiety, M, includes one of a first structure and a second structure, wherein the first structure is:

$$=$$
 R_6

wherein R₆ represents one of hydrogen, an alkyl group of 1 to 20 carbons, a semi- or perfluorinated alkyl group of 1 to 20 carbons, and CN, and wherein the second structure is:



wherein t is an integer from 0 to 3.

- 24. The method of claim 16, wherein the resist polymer further comprises at least one second monomer unit derived from a second monomer having an aqueous base soluble moiety.
- 25. The method of claim 24, wherein the second monomer comprises at least one of a fluorosulfonamide and a carboxylic acid moiety.

- 26. The method of claim 16, wherein the radiation sensitive acid generator comprises at least one of an onium salt, a succinimide derivative, a diazo compound, and a nitrobenzyl compound.
- 27. The method of claim 16, further comprising at least one of a solvent and a quencher.
- 28. The method of claim 16, wherein the solvent comprises at least one of an ether, a glycol ether, an aromatic hydrocarbon, a ketone, and an ester, and wherein the quencher comprises at least one of an aromatic amine, an aliphatic amine, and a tetraalkyl ammonium hydroxide.
- 29. The method of claim 27, wherein:

the weight of the polymer is about 1% to about 30% of the weight of the composition; the weight of the solvent is about 70% to about 99% of the weight of the composition; the weight of the additive is about 5% to about 70% of the weight of the polymer; and the weight of the acid generator is about 0.5% to about 20% of the weight of the polymer.

30. The method of claim 27, wherein:

the weight of the polymer is about 5% to about 15% of the weight of the composition; the weight of the solvent is about 85% to about 95% of the weight of the composition; the weight of the additive is about 10% to about 50% of the weight of the polymer; and the weight of the acid generator is about 0.5% to about 15% of the weight of the polymer.